

TIME-RESOLVED X-RAY DIFFRACTION INVESTIGATION OF SUPERHEATING-MELTING OF CRYSTALS UNDER ULTRAFAST HEATING

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Abstract. The maximum superheating of a solid prior to melting depends on the effective dimensionless nucleation energy barrier, heterogeneities such as free surfaces and defects, and heating rates. Superheating is rarely achieved with conventional slow heating due to the dominant effect of heterogeneous nucleation. In present work, we investigate the superheating-melting behavior of crystals utilizing ultrafast heating techniques such as exploding wire and laser irradiation, and diagnostics such as time-resolved X-ray diffraction combined with simultaneous measurements on voltage and current (for exploding wire) and particle velocity (for laser irradiation). Experimental designs and preliminary results are presented.

INTRODUCTION

Superheating is the state where the long-range order of a solid persists above its equilibrium melting temperature (T_m). It is related to the kinetics of melting – to overcome the energy barrier for solid-liquid transitions. Thus superheating is supposed to be common in melting process where heating rate (Q) also plays an important role. Appreciable amount of superheating is seldom observed in conventional low heating rate experiments ($Q \sim 1$ K/s), due to the heterogeneous nucleation at free surfaces, defects and impurities. As heating rate and heterogeneous nucleation are competing factors, superheating could be marked for ultrafast heating as in light-gas gun loading and laser irradiation. To study the materials properties (in particular melting behavior) under extreme conditions, e.g., to interpret the results of shock melting experiments ($Q \sim 10^9 - 10^{12}$ K/s), understanding the

kinetics of melting (in time t , pressure P and temperature T) is of immediate importance.

If a solid with a dimensionless nucleation energy barrier (β) is superheated at heating rate Q to a maximum temperature T_c , the maximum superheating achieved is $\theta_c = T_c/T_m$. [1] β depends on solid-liquid interfacial energy γ_{sl} , heat of fusion ΔH_m and T_m : $\beta \equiv 16\pi\gamma_{sl}^3/3\Delta H_m^2 kT_m$. The systematics[1] of maximum superheating was established as

$$\beta = (A_0 - b \lg Q)\theta_c(\theta_c - 1)^2 \quad (1)$$

where $A_0 = 59.4$, $b = 2.33$ and Q is normalized by 1 K/s. The values for parameter β are documented[1], e.g., β is about 1.5 and 8.2 for Cu and Ga, which correspond to θ_c of ~ 1.19 and 1.43 at $Q \sim 10^{12}$ K/s, respectively. Systematic molecular dynamics simulations[1] yielded results consistent with such systematics. Previous superheating experiments compare favorably

to the systematics, but the amount of superheating data is very limited.

The above systematics simply supply an upper bound to superheating. To resolve the degree of superheating in real experiments, we need to know T and T_m , and phases of the heated sample. The persistence or breakdown of the long-range order of solid can best be resolved from time-resolved (or transient) X-ray diffraction (TXD). Accurate temperature measurement is critical but challenging. In this work, we utilize exploding wire[2] and laser irradiation techniques to investigate superheating-melting behavior under various heating rates with such diagnostics as TXD, line-imaging velocity interferometry (VISAR), and voltage and current measurements. Experimental designs and preliminary results are presented. The main purpose of this work is to point out the possible directions for experimental investigation of superheating-melting behavior. The preliminary results are mostly utilized to illustrate idea rather than draw any solid conclusions.

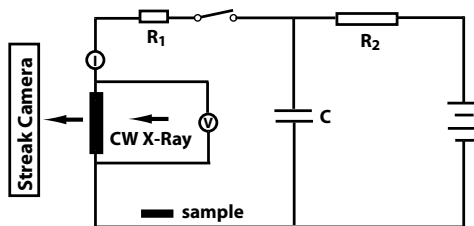


FIGURE 1. Schematic of exploding wire[2] circuit with TXD diagnostics. Metallic sample wire is subjected to ohmic heating with voltage (V) and current (I) evolutions recorded. *In-situ* TXD pattern of the sample is recorded continuously by the streak camera. X-ray source can be continuous wave (CW, e.g. from synchrotron) or pulsed.

EXPLODING WIRES

When a metallic wire of sample is subjected to discharging of a capacitor (Fig. 1), the temperature of the wire before it becomes melted, vaporized or plasma-ized, can rise to $\sim 10^3$ K in ~ 10 - $100 \mu s$ (average $Q \sim 10^7 - 10^8$ K/s) or less by ohmic heating. The high heating rate itself may induce significant superheating. A wide

range of heating rates can be obtained by varying capacity, applied voltage and resistance (Fig. 1), and the effect of heating rates can be investigated.

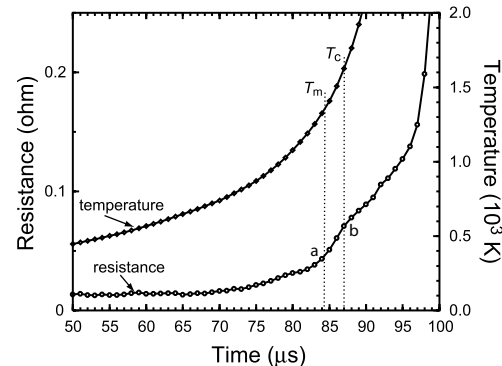


FIGURE 2. Time evolution of resistance (R , calculated from measured $V(t)$ and $I(t)$, not shown) and temperature (T) of the Cu wire during ohmic heating. This wire was 143 mm long and 0.3556 mm in radius.[3] Values of T assume solid state and Dulong-Petit limit for C_p . T_m (1356 K for Cu) is the equilibrium melting point, and T_c (~ 1600 K) the predicted maximum temperature at superheated state. Pressure is reasonably assumed to be 0 at solid states.

In the schematic of exploding wire, the current through (I) and voltage (V) across the exploding wire can be measured continuously. Thus the energy increase (ΔE) due to ohmic heating at any instant t_1 can be calculated as $\Delta E = \int_0^{t_1} V(t)I(t)dt$. Heat conduction and optical radiation to its environment, and strain energy changes can be neglected, so T_1 in the solid wire can be solved from $\int_0^{t_1} V(t)I(t)dt = \int_{T_0}^{T_1} C_p(T)dT$ where C_p is heat capacity. Temperature in the solid state (including superheated states if there are any) can be constrained (e.g. Fig. 2 for exploding Cu wire). To tell whether it is melted, one possible way is to examine the evolution of resistance $R(t) = V(t)/I(t)$ along with $T(t)$, as the electrical conductivity of liquid metal may differ from that of the solid. For example, T_c , the predicted maximum temperature of Cu (from Eq. 1 at $Q \sim 10^8$ K/s) at the superheated state, corresponds to R_b where the curvature of R starts to change, i.e. melting could

occur at the superheated state b rather than a (corresponding to T_m). Upon catastrophic melting at b , the temperature excess cannot fully compensate the required latent heat to melt the whole sample, thus only partial melting occurs at b ($\sim 46\%$) and less pronounced superheating exists thereafter.

To infer the melting instant from $R(t)$, accurate temperature dependences of C_p and $R(t)$ for solid and liquid metals are needed. There still exists possibility that equilibrium melting occurs along ab – a more direct and definitive structure information can resolve such an uncertainty. Thus we propose to measure the X-ray diffraction patterns from continuous X-ray source simultaneously with $V(t)$ and $I(t)$ (Fig. 1). We expect that TXD, $R(t)$ and $T(t)$ would allow us to examine the details of melting process in a variety of metals.

We pointed out that catastrophic melting at the limit of superheating (if there is any) at b may be only partial. The possibility of continuous equilibrium melting (also partial melting) exists as well. Partial melting raises the issue – to what extent TXD can resolve melting – which remains to be investigated. Although only melting behavior near ambient pressure (the pressure from magnetic field is negligible) is investigated with exploding wire technique, it is directly relevant to high-pressure melting.

LASER IRRADIATION

Materials such as Si, Ge, Ga, Bi and water ice have negative Clausius-Clapeyron slopes at low pressures (e.g. Fig. 3). If we preheat (or precool) such solids to a certain T slightly below ambient T_m , and shock-load to a certain P in the negative dT_m/dP regime, and samples remain in solid states, then the samples are superheated. Fig. 4 is a schematic of laser irradiation (direct laser drive or laser-driven flyer) with TXD and line-imaging velocity interferometry (VISAR) diagnostics.[4] Phase change may be registered in the particle-velocity (u_p) history (Fig. 5) reduced from VISAR record. Two streak cameras (denoted as Bragg and Laue) measuring diffraction pattern in two orthogonal directions from shocked sample (Fig. 4).

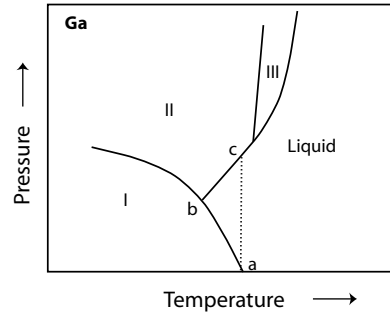


FIGURE 3. Schematic of Ga phase diagram. a denotes ambient condition ($T = 298$ K and $P = 0$. Note T_m is 303 K at zero pressure). b is the Ga I-II-liquid triple point at $T \sim 277$ K and $P \sim 1.2$ GPa. ac denotes an isotherm (298 K) to which the low- P end Hugoniot is close. If Ga sample remains crystalline at pressure below $P_c \sim 2.2$ GPa, it is certainly superheated for states on ac .

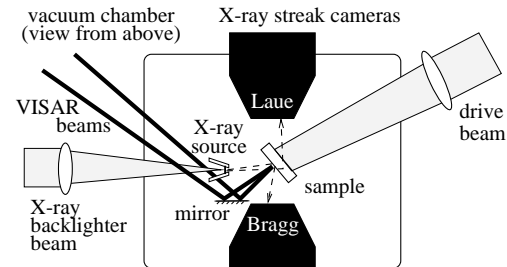


FIGURE 4. Schematic of laser irradiation with TXD and line-VISAR diagnostics. A laser beam shone on the sample surface (sample itself or coating) induces plasma, and expansion of the plasma cloud induces shocks propagating into the sample. TXD patterns are recorded in two directions by Bragg streak camera (parallel to shock wave propagation direction) and Laue camera (parallel to shock wave front).

We conducted VISAR and TXD measurements on Ga to illustrate the idea for similar experiments. Single-crystal Ga samples were grown and mounted for direct laser drive (initial temperature is ~ 298 K). VISAR (Fig. 5) and TXD (Fig. 6) measurements were separate in the preliminary shots. An elastic precursor and indication of possible phase change (melting or solid-solid) are displayed on particle-velocity history (Fig. 5). Such a possible phase change is more

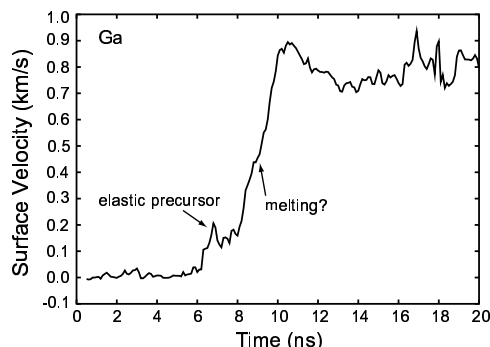


FIGURE 5. Free surface velocity history at the center of the sample (Ga) reduced from line-imaging VISAR record in a preliminary shot. No TXD was measured. The kink denoted as possible melting is more pronounced in original VISAR film record.

pronounced on un-reduced film record of VISAR. As only u_p is measured, P can only be obtained by assuming an equation of state. Laser-driven flyer experiment with measurements of flyer velocity (u_{fp}) and u_p may resolve P and shock velocity (U_s) from impedance match. In another shot, melting appears to occur on TXD at ~ 1 ns (relative time). Simultaneous measurement of u_p , diffraction pattern and u_{fp} or U_s (using stepped sample) could in principle resolve the details of melting and other phase changes.

As in the case of exploding wire, the temperature excess might not be enough to compensate the latent heat required to melt the bulk crystal at the limit of superheating (if there is any), thus only partial melting occurs. This concerns with the resolution of VISAR and TXD, i.e. the minimum portion of melting which can be resolved in TXD and VISAR recordings. In the case of Ga ($\Delta H_m = 5.6$ kJ/mol), bulk melting requires equivalent superheating (excess in T) of ~ 220 K which seems to be difficult to achieve for low P loading. But significant portion of melting could be achieved for materials with triple point at higher pressures, such as Si.

CONCLUSIONS

We present experimental designs of exploding wire and laser irradiation with time-

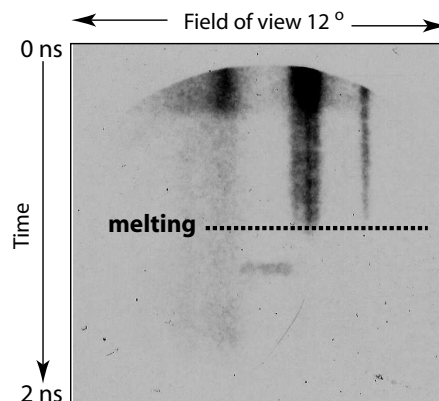


FIGURE 6. TXD pattern of laser-irradiated Ga from a separate preliminary shot. VISAR measurement was not conducted. The disappearance of diffraction pattern for the two lines to the right at ~ 1 ns (relative time) is interpreted as melting. The intensity for the diffraction line to the left is significantly dim from which no melting appears to be indicated. Further investigation is needed.

resolved X-ray diffraction diagnostics to investigate superheating-melting behavior of crystals under ultrafast heating. Preliminary results suggest that such techniques would potentially allow us to examine systematically the detailed superheating-melting process.

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